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(71) Applicant

Ultraseal International Limited

(Incorporated in Guernsey)

Unit 4, Braye Road Industrial Estate, Braye Road,  
Vale, Guernsey, Channel Islands

(72) Inventor

Peter David Young

(74) Agent and/or Address for Service

D. Young & Co.

10 Staple Inn, London, WC1V 7RD

(54) **Impregnant compositions for porous articles**

(57) The sealing of small pores in porous rigid articles is effected by impregnation with a liquid synthetic resin impregnant and subsequent curing of resin in the pores. The liquid (meth)acrylic ester impregnant composition comprises a free radical catalyst, an inhibitor and a higher alkyl (meth)acrylic ester and/or polyfunctional (meth)acrylic ester which has been obtained by transesterification in the presence of an organotitanium catalyst and from which the catalyst residue has not been removed. The catalyst residue has been found to improve sealing and thermal stability of the cured impregnant.

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IMPREGNANT COMPOSITIONS FOR POROUS ARTICLES

This invention concerns the impregnation of porous articles, particularly porous metal articles such as metal castings and sintered metal parts. However, the invention is also applicable to other porous articles such as articles of wood.

Porous metal articles frequently have to be impregnated and sealed to prevent leakage of fluid and to provide a good surface finish. One preferred impregnation technique for sealing porous metal articles comprises immersing the article in liquid impregnant under vacuum conditions in an autoclave, allowing the pressure to rise so forcing the impregnant into the pores, removing the impregnated article, washing the impregnant from the surface and curing the impregnant which remains in the pores. The article is preferably subjected to vacuum conditions before immersion in the liquid impregnant but it is also possible to immerse the article in the impregnant before drawing the vacuum in the autoclave. The washing step is desirably carried out using water and in many cases it will be desirable to include a surfactant either in the water or in the impregnant. The impregnants normally used are based on one or more esters of (meth)acrylic acid, at least some of esters being derived from polyfunctional alcohols in order to provide cross linking on curing. The impregnant will normally contain a free radical-producing curing agent such as a peroxide or azo compound and an inhibitor such as a sterically hindered phenolic compound. It is also desirable to include a small amount of metal chelating agent. Compositions catalysed by peroxy compounds and azo compounds can be heat-cured e.g. by immersing the article in hot water at say 90°C. Anaerobically curing compositions on the other hand require peroxy catalysts.

The impregnant compositions should have a sufficiently low viscosity to permit them to be drawn into the pores of the article (it should be noted in this connection that metal castings tend to have smaller pores than sintered metal articles). On the other hand, too low a viscosity encourages unwanted leaching out of impregnant from the pores during the washing step. Also, of course, water solubility has to be taken into account if an aqueous wash liquid is used. Furthermore, impregnants of low volatility clearly have to be used in order to avoid boiling off under

vacuum conditions. A low surface tension liquid impregnant is also desirable since it permits wetting of the metal in the pores and improves adhesion of the cured resin.

The storage and curing properties of the impregnant composition can be appropriately adjusted by varying the proportions of the catalyst and the inhibitor. U.K. Patent No. 1,547,801 describes various compositions which are stable at room temperature and which may be cured at 90°C in a water bath in a period from 3 to 15 minutes. Further compositions of this type are disclosed in European Patent Application No. 14062. These two documents describe examples of impregnant compositions of the type with which the present invention is concerned and give examples of monomers, catalysts and inhibitors together with the proportions in which they may be used.

The most preferred impregnant compositions with which the invention is concerned are based on polyethylene glycol dimethacrylate and tetraethylene glycol dimethacrylate (TEGMA). As explained in U.K. Patent No. 1,547,801, it is, however, desirable to include some monofunctional (meth)acrylate because the monofunctional compounds are more stable and less susceptible to anaerobic effects. Furthermore, wholly polyfunctional (meth)acrylate esters tend to shrink on curing to a greater extent than monofunctional esters which can lead to leakage problems. Polyfunctional (meth)acrylate ester resins are also more brittle so that a plasticising effect is necessary to give the necessary properties; the plasticising effect may be obtained by incorporating a conventional resin plasticiser such as dioctyl phthalate or it may be obtained by using a monofunctional (meth)acrylate comonomer. Normally the polyfunctional (meth)acrylate will be in a proportion from 2-70% preferably 10-25%. Lower monofunctional (meth)acrylates such as methyl (meth)acrylate tend to be too volatile and C10 to C14 alkyl (meth)acrylates are more preferred. It is also desirable to include a hydrophilic alkyl (meth)acrylate such as hydroxypropyl methacrylate or hydroxyethyl acrylate to facilitate washing and to improve adhesion of the cured resin.

Higher alkyl (meth)acrylates and polyfunctional (meth)acrylates are normally manufactured in practice by a

transesterification, or more correctly alcoholysis, reaction, between methyl (meth)acrylate, a suitable higher alcohol and a catalyst in a suitable proportion for effecting the reaction within a suitable time at a convenient temperature.

The higher alcohol reacts with the methyl (meth)acrylate at temperatures around 100°C (50-150°C) to produce higher alkyl (meth)acrylate and methanol, the latter being removed from the reaction zone in order to drive the reaction to completion. The alcoholysis reaction will often be carried out using a stoichiometric excess of methyl (meth)acrylate to ensure complete conversion of higher alcohol to ester. It is also common practice to include a hydrocarbon solvent such as cyclohexane or benzene in the reaction mixture to facilitate the separation and removal of the by-product methanol from the methyl (meth)acrylate reactant via an azeotropic distillation. Inhibitors, such as substituted phenols or other inhibitors, will also be included to prevent premature polymerisation of the monomers during the reaction.

Upon completion of the reaction, indicated by cessation of methanol evolution, it is usual to purify the products prior to use first by removing any volatile materials such as excess methyl (meth)acrylate by distillation under vacuum and then to vacuum distil the product itself. Should the product have such a high boiling point as to render distillation difficult or impossible without polymerisation the product would be purified by treatment in the liquid state to adsorb and remove catalyst residues or coloured bodies etc.

Treatment can also take a form whereby catalyst residues are reacted to render them insoluble so that they precipitate from the product and can be removed by a suitable means such as filtration, centrifugation, or adsorption onto charcoal prior to filtration. Such purification stages are both time consuming and lead to yield losses and therefore add significantly to the cost of manufacturing higher alkyl (meth)acrylates and polyfunctional (meth)acrylates.

We have now found, according to the invention, that it is not necessary to remove the catalyst, and that the higher alkyl or polyfunctional (meth)acrylate can be used in the condition that appertains

after reaction and removal of by-products such as excess methyl (meth)acrylate and methanol. The use of higher alkyl and polyfunctional (meth)acrylates without removal of the catalyst in an impregnant composition lowers the surface tension of the composition leading to improved wetting and adhesion. Cured impregnants also show greater stability when subjected to elevated temperature conditions such as 200°C. The omission of the step of removing the catalyst also reduces the cost of producing the impregnant composition.

The catalyst normally used for the alcoholysis transesterification process is an organometallic titanium compound, particularly tetra lower alkyl orthotitanate such as tetra isopropyl titanate or tetra n-butyl titanate, or the titanate of the relevant higher alcohol could also be used. Titanates are effective transesterification catalysts as they do not promote side reactions and only require moderate temperatures.

Thus according to one aspect of the invention there is provided a liquid (meth)acrylic ester impregnant composition for porous articles comprising an organometallic titanium compound which is preferably soluble therein, preferably a tetra alkyl orthotitanate or the titanium compound derived therefrom during the course of transesterification. In this connection, it has been found that adding a similar amount of titanium catalyst to an impregnant composition made from purified monomers from which the original catalyst has been removed is generally less satisfactory e.g. because the added titanium compound tends to precipitate out.

According to another aspect, the invention provides a process for preparing a liquid (meth)acrylic ester impregnant composition which comprises reacting a lower alkyl (meth)acrylate with a higher alcohol in the presence of an organo titanium catalyst to provide a higher alkyl (meth)acrylate, and adding a polyfunctional (meth)acrylate and/or a hydroxyalkyl (meth)acrylate to the reaction product without removal of the organo titanium catalyst.

According to another aspect, the invention provides a process for preparing a liquid (meth)acrylate ester impregnant composition which

comprises reacting a lower alkyl (meth)acrylate with a polyfunctional alcohol, glycol or polyalkylene glycol in the presence of an organo titanium catalyst to provide a polyfunctional (meth)acrylate and adding a higher alkyl (meth)acrylate and/or a hydroxyalkyl (meth)acrylate to the reaction product without removal of the organo titanium catalyst.

According to another aspect, the invention provides a process for preparing a liquid (meth)acrylate ester impregnant composition which comprises reacting a lower alkyl (meth)acrylate with a higher alcohol and a polyfunctional alcohol, glycol, or mixtures thereof, either alone or together, in the presence of an organo titanium catalyst to provide a mixed (meth)acrylate ester composition and adding one or more other desirable (meth)acrylate esters such as hydroxyalkyl (meth)acrylates, polyalkylene glycol mono(meth)acrylates, (meth)acrylate containing oligomers etc.

Our experiments have shown that it is desirable for the impregnant to contain 50-1000 ppm Ti derived from the transesterification catalyst.

#### EXAMPLES

A range of impregnation compositions (sealants) was prepared using monomers prepared and purified to a normal commercial quality and also monomers according to this invention in which the tetra-isopropyl titanate esterification catalyst was allowed to remain in the monomer. These sealants were subjected to a series of evaluation tests as detailed below.

#### SEALING PERFORMANCE

Annular sintered iron test rings of 20% pore volume and dimensions 25mm outside diameter, 14mm inside diameter, and 14mm height were impregnated using a wet vacuum technique. This consisted of immersing the rings in the sealant and subjecting them to vacuum of 5 mbar for 10 minutes to remove air from the porosity, and releasing the vacuum to atmospheric pressure to fill the pores with sealant. The rings were removed from the sealant, allowed to drain, washed with water and the sealant polymerised in the pores by immersing the rings in hot water at 90°C for 10 minutes. The rings were pressure tested under water with

air at 90 'psi' pressure and assessed for leaks on a 0-5 scale with 0 signifying no leakage and 5 a level of leakage at which castings (as opposed to tests rings) might not be 100% sealed.

#### THERMAL STABILITY

Small samples of sealant were polymerised in 3mm diameter test-tubes for 30 minutes at 90°C. The samples were removed from the test-tubes and the percentage loss in weight determined after 1 hour and 24 hours, at 150°C and 200°C. The percentage loss in sealant weight was also determined under the same conditions but using impregnated sintered metal test rings as described above.

#### GEL TIME

A 5ml sample of sealant was heated in a test-tube in a water bath at 90°C. The time taken for polymerisation to proceed to a point where the tube and its contents could be lifted from the water bath on the end of a piece of wire immersed in the sealant was determined.

The following three sealant formulations were prepared in parts by weight.

	<u>1</u>	<u>2</u>	<u>3</u>
Hydroxypropyl methacrylate	65	65	65
Lauryl methacrylate	15	--	--
Lauryl methacrylate (inc. catalyst residue 600ppm as Ti)	--	15	15
Triethylene glycol dimethacrylate	20	20	--
Triethylene glycol dimethacrylate (inc. catalyst residue 1000ppm as Ti)	--	--	20
Azobisisobutyronitrile	0.4	0.4	0.4
Inhibitor (sterically hindered substituted phenol)	0.15	0.15	0.15
Residual Ti in ppm (based on whole formulation)	0	90	290



Results of the various tests are given in the table below:-

	<u>1</u>	<u>2</u>	<u>3</u>
Gel time @ 90°C Min	1.25	1.0	1.2
% Wt loss at 200°C			
Test piece (1) 1 Hr	3.2	3.3	1.7
(2) 24 Hrs	51	32	9.0
Test Ring (1) 1 Hr	7.4	5.1	6.3
(2) 24 Hrs	56	26	21
Test Ring Sealing			
Rating: After polymerisation	3	2	0
After 1 Hr @ 150°C	3+	3	0
After 24 Hrs @ 150°C	4	4	0
After 1 Hr @ 200°C	5	4	0
After 24 Hrs @ 200°C	5+	4+	0

The results quoted are the average of duplicate tests and they clearly indicate the superior sealing performance and improved thermal stability of the sealants of the invention.

CLAIMS

1. A liquid (meth)acrylic ester impregnant composition comprising a free radical catalyst, an inhibitor and a higher alkyl and/or polyfunctional (meth)acrylic ester which has been obtained by transesterification in the presence of an organotitanium catalyst and from which the catalyst residue has not been removed.
2. A composition according to claim 1 which is room temperature-stable and hot water-curable.
3. A composition according to claim 1, 2 or 3 wherein said catalyst comprises tetra-isopropyl titanate.
4. A composition according to any preceding claim which contains 50-1000 ppm of Ti.
5. A vacuum impregnation process in which a porous article is vacuum impregnated with a composition according to claim 1, 2, 3 or 4, excess impregnant is removed by washing and the impregnant in the pores is cured by heating.
6. A composition according to claim 1 substantially as described as Formulation 2 or Formulation 3.
7. A process for preparing a liquid (meth)acrylic ester impregnant composition which comprises reacting a lower alkyl (meth)acrylate with a higher alcohol in the presence of an organotitanium catalyst to provide a higher alkyl (meth)acrylate, and adding a polyfunctional (meth)acrylate and/or a hydroxyalkyl (meth)acrylate to the reaction product without removal of the organotitanium catalyst.
8. A process for preparing a liquid (meth)acrylate ester impregnant composition which comprises reacting a lower alkyl

(meth)acrylate with a polyfunctional alcohol, glycol or polyalkylene glycol in the presence of an organotitanium catalyst to provide a polyfunctional (meth)acrylate and adding a higher alkyl (meth)acrylate and/or a hydroxyalkyl (meth)acrylate to the reaction product without removal of the organotitanium catalyst.